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Cluster Rule Impact on Recovery Boiler Operations: Chloride and Potassium Concentrations in the Kraft Liquor Cycle

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CLUSTER RULE IMPACT ON RECOVERY BOILER OPERATIONS: CHLORIDE AND POTASSIUM CONCENTRATIONS IN THE KRAFT LIQUOR CYCLE

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ABSTRACT

The proposed EPA cluster rules require the implementation of Best Management Practices (BMPs) to contain pulp and liquor spills. The proposed rules also impose strict final effluent COD limits which imply closed screen rooms and improved washing to minimize carryover to the bleach plant. In essence, the cluster rules require that the liquor cycle be closed to a higher degree than has typically been practiced.

The melting point of ash generated in recovery boilers is influenced by the chloride and potassium concentrations in the fired liquor. An increase in either chloride or potassium concentrations can result in a lower ash melting point, leading to accelerated plugging in the upper furnace sections and subsequent downtime required for water washing the boiler.

Computer simulation was used to predict the effect of increased liquor cycle closure on the concentrations of chloride and potassium in the kraft liquor cycle. A sensitivity analysis has been performed to relate the concentrations of chloride and potassium in the liquor cycle to inputs with the wood and water, fume enrichment in the recovery boiler, and purging of recovery boiler electrostatic precipitator dust.

The analysis revealed that wood species, recovery boiler enrichment ratio, and liquor spills have the greatest influence on the concentrations of chloride and potassium in the liquor cycle. Chloride and potassium concentrations were found to build up substantially with very tight spill collection. However, purging a small fraction of the precipitator dust results in substantially lower concentrations of chloride and potassium.

INTRODUCTION

The papermaking process has been perfected over a 300-year span in which water was an abundant resource to be freely used and discarded. Recently the pulp and paper industry has begun to view its water resources as both a limited and valuable commodity. This change in philosophy has not come easily, nor has it been entirely self motivated. Most of the change in the industry's attitude towards water use has been motivated by increasingly restrictive environmental regulations on pollutant loads in pulp and paper mill waste-water effluents.

In response to these regulations, and in hopes of avoiding future environmental concerns, attempts are being made to increase mill closure by reusing water internally within the mill processes. Reuse of water within the mill can reduce both fresh water makeup requirements and pollutant loads of waste-water discharges. However, a number of operational problems arise as mills close up their water circuits. One such problem is caused by the accumulation of chloride and potassium in the recovery cycle.

Potassium and chloride are alkali soluble ionic elements which are always present in kraft pulp mill process streams. Under normal operating conditions, chloride and potassium enter the mill with the wood fed to the digester and to a smaller degree with the water and makeup chemicals used in pulping operations. These elements then pass through the system without causing significant problems and leave the cycle with the pulp or with spilled liquor. In contrast, in pulp mills with tightly closed water circuits, chloride and potassium concentrations can build up to 4 to 12 times that of mills with open water circuits.[1]

Increased chloride and potassium concentrations in the kraft liquor cycle can result in accelerated corrosion, boiler plugging, and ring formation in the lime kiln. Boiler plugging is a concern to many mills because of the production loss incurred when the recovery boiler is shut down for a water wash.

To determine the impact of increased liquor cycle closure on the concentrations of chloride and potassium in the kraft liquor cycle, a steady-state computer simulation of a bleached kraft mill was created using WinGems™. The simulated mill consisted of pulping in a continuous digester, brown stock washing and screening, liquor evaporation and combustion, liquor recausticizing and lime calcining. A block diagram of the simulation can be found in the appendix.

A sensitivity analysis has been performed with the simulation to relate the concentrations of chloride and potassium in the liquor cycle to wood and water inputs, fume enrichment in the recovery boiler, and purging of recovery boiler electrostatic precipitator dust.

Recovery Boiler Deposits

Deposits found on recovery boiler tubes are formed by two sources, carryover and vaporization-condensation (dust).[2] Carryover consists of particles of burned black liquor which are carried to the heat exchange surfaces of the upper furnaces rather than settling on the smelt bed. Dust refers to compounds which are volatilized in the lower portion of the furnace and later condensed on the cooler heat exchange tubes in the upper furnace. The composition of dust and carryover is not identical. Deposits and electrostatic precipitator dust are a mixture of both carryover and dust. Dust usually forms in the upper superheater, generator bank, and economizer rather than the lower superheater because temperatures in the lower superheater are too high for condensation to occur. [3]

The rate of formation of deposits on recovery boiler heat exchange surfaces is a function of the amount of liquid phase present in the deposit. The amount of liquid increases with increasing temperature. However, below a critical minimum temperature, the deposits will have no liquid phase and will act as solid particles. This minimum temperature is known as the first melting temperature.[4]

When deposits contain between 15% and 70% liquid phase, they will be sticky and cause rapid plugging if not removed. The temperature which results in a sticky deposit with 15% liquid phase is known as the sticky temperature. Accordingly, the temperature resulting in a deposit with 70% liquid phase is know as the flow[5] temperature or the radical deformation temperature[6].

Because the flue gas temperature decreases as it passes through the various tube sections, the sticky temperature and the flow temperature define a region in which deposits are expected to be worse. Deposits in this region will contain enough moisture to adhere to the boiler tubes, but not enough to freely flow off the tubes. These deposits will grow into the hot flue gases until their temperature reaches the radical deformation temperature. [6]

Chloride and potassium compounds such as KCl, NaCl, and KOH have vapor pressures which are higher than sodium sulfate[2] which result in their preferential volatilization from the smelt bed into the dust stream. As with other fume particles, the chloride and potassium compounds condense on the cooler heat exchange surfaces of the upper furnace. As a result of this preferential volatilization, chloride and potassium accumulate in the dust portion of the deposits and in the precipitator catch rather than the carryover portion of the deposits.

Chloride has been found to lower both the sticky temperature and the radical deformation temperature of recovery boiler fireside deposits.

The effect of increasing potassium concentrations on the deposit sticky temperature is similar to that of chloride but less pronounced. Potassium works in conjunction with chloride to decrease the deposit sticky temperature and radical deformation temperature. At low chloride concentrations, potassium has very little effect on deposit sticky temperature. However, when the molar fraction of chloride (Cl/(Na+K)) exceeds about 10%, potassium significantly lowers the sticky temperature.

Chloride and Potassium Concentrations

The concentration of chloride and potassium in the liquor cycle can be expressed in many ways. However, a convention adopted by previous authors[3,4,5,6] is to express chloride and potassium concentrations as molar percent ratios relative to sodium and potassium. The molar percent ratio of chloride is CL/(Na+K) and that of potassium is K/(Na+K). The advantage of using these molar ratios is that they are independent of liquor density, solids content, and organic/inorganic ratio. In addition, use of molar percent ratios allows for direct comparisons of chloride and potassium concentrations in liquor, smelt, deposits, and dust.[7]

Mechanism of Accumulation

Most of the chloride and potassium enters the liquor cycle with wood and with makeup chemicals. There are no intentional purges for alkali-soluble elements in a typical kraft mill operation. Most of the alkali-soluble ions leave the liquor cycle with the pulp off the last brown stock washer and with liquor spills or other unintentional pulp and liquor losses. A small portion of chloride and potassium is purged with the tall oil, boiler flue gas, grits, dregs, lime, etc.

One of the economic advantages of the kraft process is a high level of cooking chemical recovery. To illustrate the impact of recycle (or recovery) on trace contaminate build up, the material balance of a simple single-recycle-loop process is shown in Figure 1.

The accumulation factor graphed on the Y axis is the multiplier which represents the concentration of trace contaminates divided by the input concentration at the given recovery rate. For example, if the recovery process is 95% efficient, then one should expect there to be 20 times the amount of contaminants in the liquor cycle as in the input stream. At 99.9% recovery, the liquor cycle concentration is 1000 times that of the input stream. Clearly, as the

recovery and recycle of kraft liquors increases, the concentration of trace contaminants can rise dramatically. Since the economics favor a high recovery of process chemicals, it is desirable to have high liquor recovery. However, the accumulation of trace elements requires a controlled purge. It is desirable to have the purge enriched in the trace elements relative to the process chemicals.

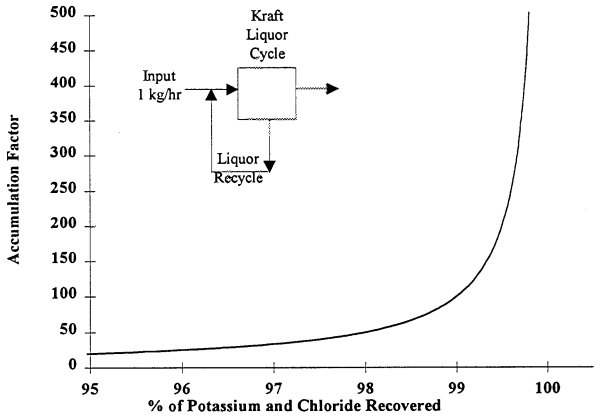

Figure 1: Mechanism of chloride and potassium build up in the kraft liquor cycle.

RESULTS AND DISCUSSION

The following assumptions were used in all simulations, unless otherwise noted:

1. Approximately 8% of the fired solids ends up in the ESP dust from either volatilization or particle entrainment.
2. The electrostatic precipitator is 99.5% efficient.
3. The overall brown stock washer Norden E_{10} Factor is 28.
4. The chloride and potassium enrichment ratios increase or decrease together.
5. Increased Na_2SO_4 liquor losses can be approximated by purging proportional amounts of weak black liquor and weak wash.

Equivalent Loads

The effect of six variables on the concentration of chloride and potassium in the liquor cycle were examined. The variables considered were:

- K and Cl concentrations in the wood supply
- K and Cl concentrations in the fresh water
- K and Cl concentrations in the makeup chemicals
- K and Cl boiler enrichment ratios
- Brown stock washing efficiencies
- Soda Losses (liquor spills)

The accumulation factor described previously was determined for both chloride and potassium in the simulation. This was done for each input source to determine if the location of the input source was important or if chloride and potassium added in one location would build up to exactly the same level as chloride and potassium added at a different location.

The results of this investigation are found in Table 1. From Table 1, one can see that potassium in the liquor cycle will be about 24 times that in the wood chips and chloride will be about 28 times that in the wood chips. This is true not only for wood chips but for all inputs except fiberline water. The reason is that a large portion of the wash water applied to the last brown stock washer leaves with the mat and does not enter the liquor cycle. The accumulation factors for chloride and potassium are different because a portion of the potassium is sorbed to the pulp and is therefore purged with the exiting pulp to a greater extent than chloride.

	Accumulation Factor	
	K	Cl
Source	(kg in B.L.)/(kg input)	
Wood Chips	24.3	28.3
Fiberline Fresh Water	3.2	9.8
Recovery Fresh Water	23.1	27.2
Makeup Caustic	24.6	28.6
Makeup Saltcake	23.9	27.8
Makeup Lime	24.1	28.1

Table 1: Accumulation factors for liquor cycle inputs of potassium and chloride.

Equivalent loads were also calculated for possible chloride and potassium inputs at base case conditions (no ESP dust purge, E_K=1.5, E_{CL}=2.5). The equivalent load of an input is a measure of the relative importance of the input. It is defined as the product of the accumulation factor of the system, the average flow rate of the input, and the average concentration of potassium or chloride in the input stream. The units of equivalent load are therefore kg (K or Cl)/hr in the liquor cycle. Table 2 lists the equivalent loads for the various liquor cycle input streams.

	Avg. Flow	Avg. Concentration		Equivalent loads	
		K	Cl	K	Cl
Source	mt/hr	ppm	ppm	(kg/hr)	(kg/hr)
Wood Chips	139	657	67	2221	263.5
Fiberline Fresh Water	568	2	20	3.62	110.7
Recovery Fresh Water	291	2	20	13.46	158.1
Makeup Caustic	1.2	700	1000	20.59	34.17
Makeup Saltcake	1.0	100	5000	2.42	141.2
Makeup Lime	0.0006	100	100	0.001	0.002

Table 2: Equivalent loads

By comparing the calculated equivalent loads of the various potassium inputs, we can see that potassium input with the

wood chips is over 200 times more important than potassium input to the fiberline with fresh water. In the case of potassium, wood chips have at least two orders of magnitude more effect on the liquor cycle concentration than does any other input source. Therefore even relatively large changes in potassium concentrations in the makeup chemicals will not significantly alter the potassium concentrations in the liquor cycle.

However, in the case of chloride, both makeup water and chemicals have nearly the same effect on liquor cycle concentrations as do wood chips. Despite this, the effect of changing chloride levels in the makeup chemical streams was not investigated in this study. It was assumed that changing chloride concentrations in makeup streams will have similar effects to changing chloride concentrations in wood chips. This assumption is supported by the fact that the equivalent loads for these sources are very similar. In addition, chloride levels in makeup chemicals and water streams should be fairly constant and will therefore tend to establish a base level of chloride in the system. In contrast, the chloride concentration in the wood source varies widely by species and with the degree of residual bark remaining in the chips. It therefore cannot be assumed to be constant.

Brown Stock Washer Efficiency

Chloride and potassium concentrations in the liquor cycle increase logarithmically as the total brown stock washing fiberline efficiency increases (as measured by the Norden efficiency factor at a normalized washer discharge consistency of 10%, E_{10}). An asymptotic limit is reached for a total wash line E_{10} of greater than 25.

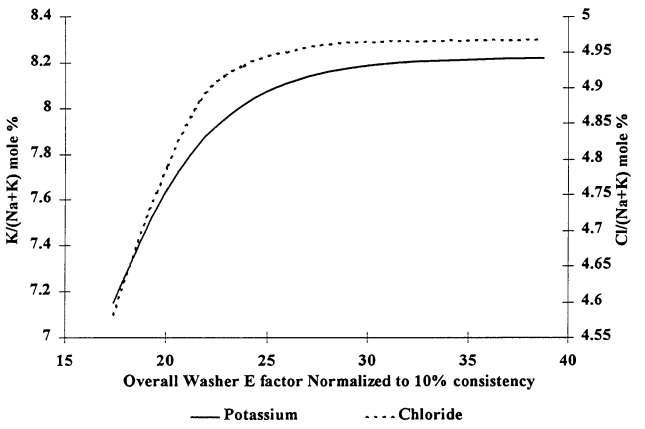

Figure 2: Chloride and potassium concentrations in ESP dust as a function of overall brown stock washing Norden efficiency factor, E_{10}.

Figure 2 illustrates this logarithmic increase as washing efficiency is improved and less chloride and potassium is purged with the pulp off the last washer. The significance of this is that if a mill's current brown stock washing has an overall E_{10} factor of less than 25 (without O_2 delignification) then improving washing efficiency to reduce washable solids carryover (COD) can have a noticeable impact on the chloride and potassium concentrations in the liquor cycle.

The effects of brown stock washing were eliminated from further analysis in the study by assuming a high brown stock washing efficiency, E_{10}, factor of 28.

Effect of Spill Collection

Figures 3 and 4 show chloride and potassium concentrations as functions of soda loss expressed in equivalent lb of Na_2SO_4 rather than spills directly. Soda loss is easily measured and is directly proportional to the degree of liquor spills when all other sources of sodium losses are held constant, as was done in this study.

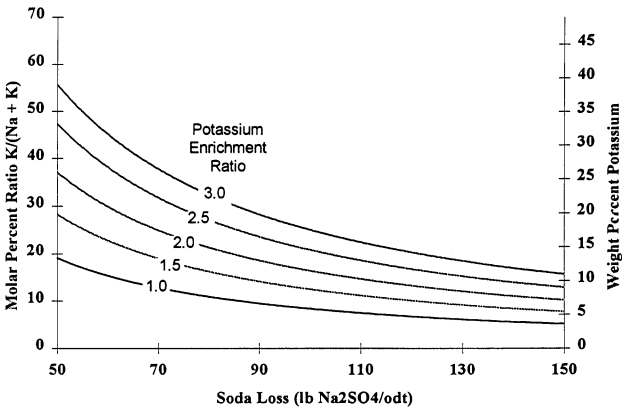

Figure 3: Effect of spill collection on the ESP dust potassium concentration. Hard maple used as the wood source.

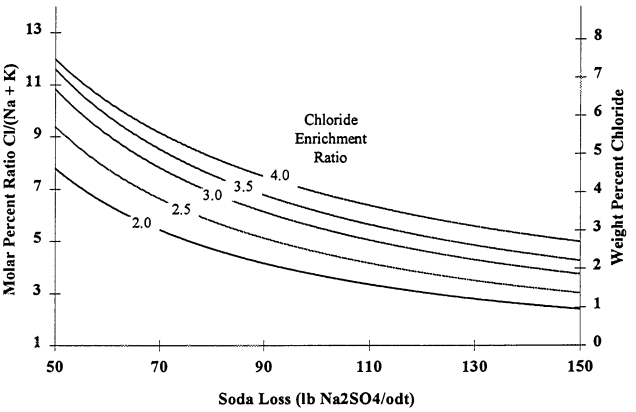

Figure 4: Effect of spill collection on the ESP dust chloride concentration. Hard maple used as the wood source.

Figures 3 and 4 show that spill collection has a large impact on the concentration of chloride and potassium in the ESP dust. This is especially true when the soda loss drops to below 100 lb Na_2SO_4 equivalent/odtpd. The significance of this finding is that improved spill collection systems should decrease soda losses and also chloride and potassium losses. The simulation predicts that chloride and potassium concentrations in the precipitator dust could increase by up to a factor of four when soda loss is decreased by half.

Effect of Enrichment Ratio

The chloride and potassium enrichment ratios are defined as the molar ratio of chloride and potassium in the ESP dust to that in the strong black liquor.

$$E_K \equiv \frac{K}{Na + K_{Dust}} \Big/ \frac{K}{Na + K_{BLS}} \quad (1)$$

$$E_{Cl} \equiv \frac{Cl}{Na + K_{Dust}} \Big/ \frac{Cl}{Na + K_{BLS}} \quad (2)$$

The chloride and potassium enrichment ratios are basically a measure of the degree of preferential volatilization of these compounds to that of sodium compounds. The enrichment factor is determined by boiler operating parameters which effect volatilization such as temperature and SO_2 concentration. Boilers which operate at conditions which enhance volatilization (high temperature, oxygen content, and SO_2 concentration) should be expected to have significantly higher chloride and potassium concentrations in the ESP dust.

Effect of Wood Species

Species	Potassium (ppm)	Chloride (ppm)
Douglas Fir *Pseudotsuga menziesii*	657[8]	67[9]
Hard Maple *Acer saccharum*	990[9]	82[9]
White Oak *Quercus alba*	1162[10]	15[10]

Table 3: Species and concentrations used

In this study, three tree species were examined. Figures 5 and 6 show the effect of wood species on chloride and potassium concentrations in the liquor cycle. The chloride and potassium concentrations in these species were taken from literature.[8,9,10] Table 3 lists these species and their corresponding potassium and chloride concentrations.

Figures 5 and 6 show that the concentration of chloride and potassium in the precipitator dust is almost proportional to that in the incoming wood. This suggests that mills which obtain a large portion of their fiber supply from high chloride and potassium sources such as whole tree chipping, chips from certain hardwoods, and sea floated logs should expect to have more problems with boiler deposits especially if liquor spills are minimized.

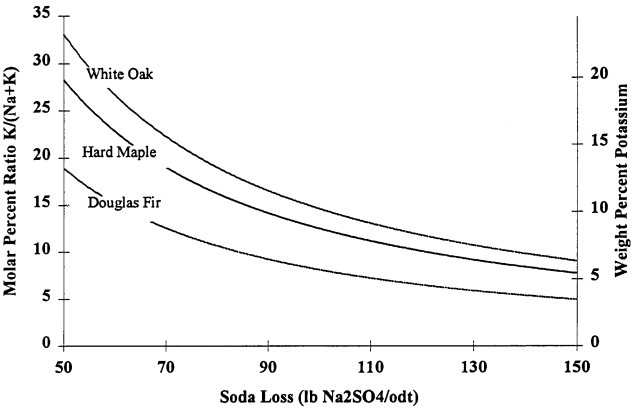

Figure 5: Effect of wood species on potassium concentrations. Boiler enrichment ratio set to 1.5.

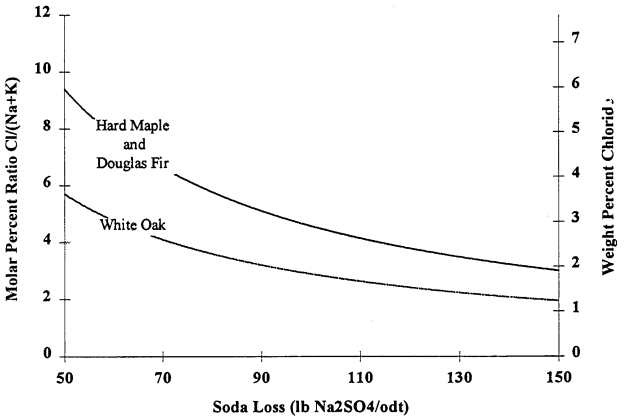

Figure 6: Effect of wood species on chloride concentrations. Boiler enrichment ratio set to 2.5.

Purge Analysis

ESP dust purging has long been thought to be an effective and easy way to control chloride and potassium concentrations. However, the economics of purging dust is impacted by the accompanying loss of saltcake which most often must be made up with purchased chemicals. Purging ESP dust has the lowest economic penalty as a purge stream because, compared to other liquor cycle streams, it is enriched in chloride and potassium relative to saltcake.

Figure 7 shows the effect of different purge levels and base soda loss levels on the potassium concentration in the ESP dust. The base saltcake loss plotted on the X axis is simply the sodium loss due to factors other than dust purging such as spills. This plot also shows how a small purge of dust can reduce the potassium concentration enough to

compensate for a fairly significant reduction in liquor spills. For example, purging only 2.5% of the ESP dust would allow a mill which currently had a base soda loss of 100 lb Na_2SO_4/odtpd to drop to 90 lb Na_2SO_4/odtpd without increasing their ESP potassium concentration.

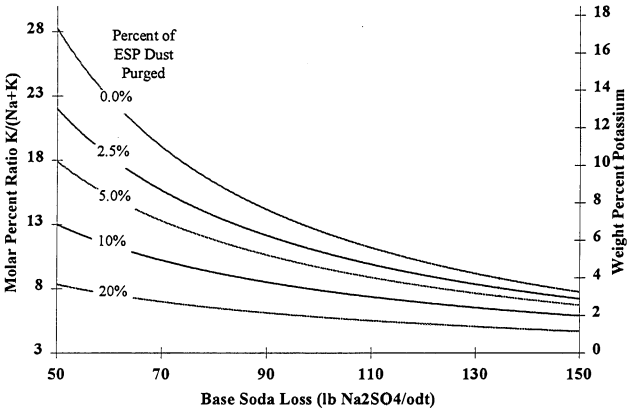

Figure 7: Effect of dust purging on potassium concentration. Hard maple used as wood source

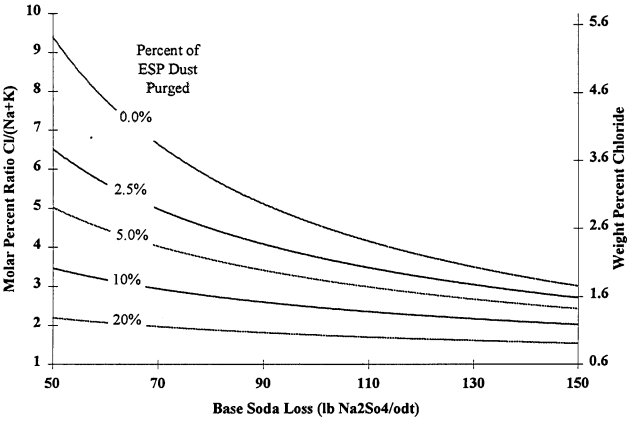

Figure 8: Effect of dust purging on chloride concentrations. Hard maple used as wood source.

The effect of dust purging on the chloride concentration in the precipitator dust is shown in figure 8 and is even more dramatic than that of potassium. For example, using the same base case mill with a base soda loss of 100 lb Na_2SO_4/odtpd, purging 2.5% of the precipitator dust would allow the mill to tighten up spills to about 80 lb Na_2SO_4/odtpd without raising the chloride concentration in the ESP dust.

Figure 8 also shows that increasing the amount of dust purged yields a diminishing decrease in chloride and potassium concentrations in the ESP dust. For example, at a base soda loss of 70 lb Na_2SO_4/odtpd, increasing the dust purge from 0 to 5% will drop the molar ratio of chloride by 2.6%. However, increasing the purge by another 5% yields only an additional 1.1% drop in the chloride molar ratio.

As one may expect, the effectiveness of purging ESP dust to remove chloride and potassium will be greatly enhanced if the boiler has high chloride and potassium enrichment ratios. Except were noted, the chloride and potassium enrichment ratios in this study were maintained at 2.5 and 1.5 respectively.

Dust Purging and Soda Loss

In the previous discussion of dust purging, base soda loss was used to measure the effect of spills. This is because purging precipitator dust causes a significant additional loss of sodium. Figure 9 shows this incremental soda loss as a function of the level of dust purging at three different ash generation levels. As shown in Figure 9, soda loss depends on the fraction of black liquor which ends up in the precipitator dust.

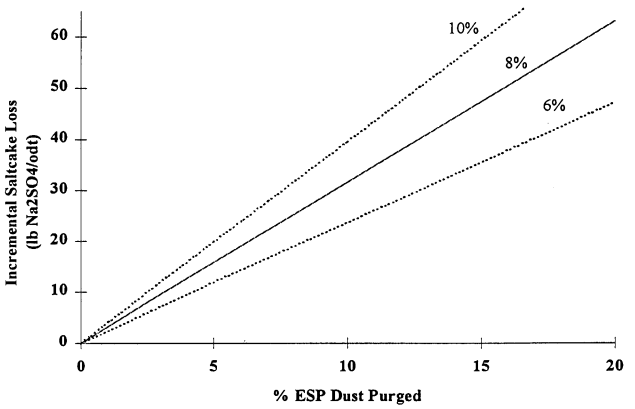

Figure 9: Effect of dust purging on incremental saltcake loss at various ash generation levels.

For a boiler with an E_K=1.5, an E_{Cl}=2.5, and a ash generation rate of 8% of fired solids, soda losses are about 3.2 lb Na_2SO_4/odtpd for every 1% of dust which is purged. This figure is dependent on enrichment ratios as well as the fraction of fired solids which end up as dust in precipitator. In this study, approximately 8% of the total fired solids (inorganic and organic) was generated as dust. Actual boiler dust generation rates will range from 5-10% of fired solids.

Soda loss due to dust purging can be minimized by recovering the sodium sulfate from the purged dust with a process which uses selective leaching or crystallization. These processes take advantage of the higher solubility of chloride and potassium salts over that of sodium sulfate.

Mills which are recovery boiler limited and are shipping black liquor usually get an effective purge of chlorides and potassium by exchanging liquor. If green or white liquor is returned on a equivalent volume basis (truck per truck) the black liquor shipping mill has a net purge of chemical to the receiving mill, since green or white liquor has a lower equivalent chemical concentration compared to strong black liquor.

If a black liquor receiving mill can tolerate a higher input level of chloride and potassium, the black liquor shipping mill could increase its effective purge by not receiving any green or white liquor back in exchange. While the pulping chemical makeup for the shipping mill would go up, the net chemical makeup for the two-mill system would be constant. For sister mills in the same company, this may be a more economical method of purging chlorides and potassium when compared to dumping ESP dust.

Recovery Boiler Plugging

Figure 10 shows the effect of chloride and potassium on deposit thermal properties. This graph was made by interpolating plots obtained in this study and those obtained by Tran.[3] Typical enrichment ratios and ion inputs with wood and water are assumed. Figure 10 shows that closing the water system by reducing the liquor spills from approximately 150 lb Na_2SO_4/odtpd to 70 lb Na_2SO_4/odtpd results in an enlarged region of sticky deposits which spreads farther into the boiler bank because the chloride and potassium concentrations have increased.

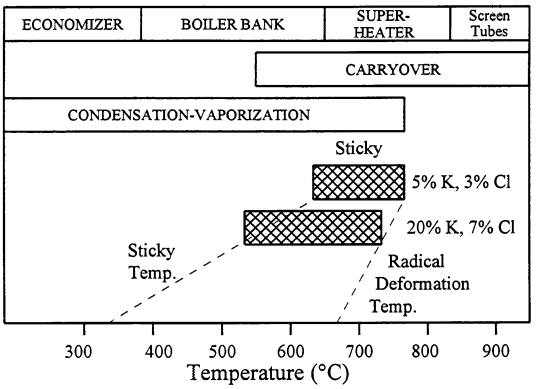

Figure 10:Summary of effects of chloride and potassium on deposit thermal properties

Conclusions

For the typical kraft mill, wood is the only significant input source of potassium, and nominal increases of potassium concentrations in water or makeup chemicals will not have a significant effect on potassium concentrations in the liquor cycle.

Chloride concentrations in wood, water, and chemical makeup can all significantly effect the chloride concentration in the liquor cycle. Mills which obtain a large portion of their fiber supply from high chloride and potassium sources should expect to have more problems with boiler plugging.

If a mill's total brown stock washing line (without O_2 delignification) has a Norden wash efficiency (E_{10}) of less than 25, then improvements in washing efficiency can drive up the chloride and potassium in the liquor cycle.

Improved spill collection systems will increase chloride and potassium concentrations and decrease soda losses in the liquor cycle.

A purge of electrostatic precipitator dust can reduce the chloride and potassium concentrations to compensate for a increase mill closure but usually at an increased saltcake makeup cost.

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APPENDIX: Simulation Block Diagram